

Dechlorination of Monochlorobenzene by Using Electrochemical Method

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Abstract

A new dechlorination system was carried out by electrolysis of a *N,N*-dimethylformamide solution containing a supporting electrolyte in a one-compartment cell fitted with a platinum cathode and a metal anode. Monochlorobenzene as a substrate was dechlorinated to benzene in this system, and the product was analyzed by gas chromatograph. Effect of temperature, type of anode material and solvent was investigated and it was also found that the rate and current efficiency for the benzene production were greatly improved when naphthalene was used as a mediator. In the presence of naphthalene, the reduction of chlorobenzene occurs indirectly compared to its direct reduction at the platinum cathode to give complete dechlorination.

Keywords: Dechlorination, monochlorobenzene, electrolysis, mediator, naphthalene.

Introduction

A large number of chlorinated aromatic compounds are environmental pollutants. The key step in their detoxification and destruction is dechlorination. One approach to dechlorination is the use of chemical reducing agents, however this requires elevated temperatures and long reaction times [1-3]. In many cases one promising method of solving ecological problem posed by chlorinated organic compounds (COC) is electrochemical reductive dehalogenation. This method offers an alternative route through cathodic reduction of carbon-chlorine bond under mild conditions which does not require the handling of reactive chemicals or the use of elevated temperature. As a result, the dechlorinated products formed, having much less toxic properties, could be disposed by more convenient and economic manner. Moreover, the electrochemical method is often quite cheap, technically flexible and really allows COC dechlorination. One advantage of this process is that it does not produce a residue, which in turn is difficult to dispose of.

However, the most of the works reported in literature were done with the cathode materials such as mercury [4-6] or lead [7-8]. These cathode materials showed high dechlorination efficiencies but, on the other hand, were unpleasant from the environmental viewpoint. Nevertheless, these studies yielded a lot of data about the mechanism and the possibility, in principle, of processes of this kind. On the other hand, indirect reduction of chlorinated and brominated compounds in the presence of organic mediators has been thoroughly studied by a number of research groups, usually as a technique for obtaining electrochemical parameters which are otherwise difficult to determine [9]. It also has been established in the literature that the limiting step in irreversible reduction of halogen organic compounds is, as a rule, electron transfer.

In the research reported in this paper, we have studied the optimum conditions of electrochemical reduction of chlorobenzene in simple electrolysis equipment in the present and absence of naphthalene as a mediator in order to remove the chlorine completely from that compound.

Experimental

In the experiments, a DMF solution (15 ml) containing 0.1M Et_4NClO_4 and naphthalene (1.2 mmol) were placed in a one-compartment cell fitted with a platinum plate cathode ($2 \times 2 \text{ cm}^2$) and a zinc plate anode ($2 \times 2 \text{ cm}^2$). Electrolysis was carried out at room temperature at a constant current of 60 mA/cm^2 under nitrogen atmosphere. During the course of electrolysis the solution was sampled and analyzed by gas chromatograph.

Result and Discussion

Direct electrochemistry. The first approach taken was to carry out direct electrolysis at 0°C without any mediator present in the solution. Table 1 shows that 74% of chlorobenzene was reduced to benzene after 6 F/mol of current were passed. However, no significant differences were found even after passing about 10 F/mol.

Table 1. Electroreduction of Chlorobenzene

Current Passed (F/mol)	Yield* (%)
2	65
4	73
6	74
10	77

* Determined by GC with tetralin as a standard material.

The fact that the use of mediators allows the electrolysis to be carried out at a less negative potential, which leading to a higher reaction current efficiency, let the authors to add naphthalene in this reaction. Moreover, the authors was successfully prepared highly reactive zinc metal when naphthalene was used as a mediator and the reactive zinc metal thus prepared was used in efficient cross-coupling reactions of ethyl 2-bromoacrylate with various aryl halides [10].

Mediated dechlorination. Naphthalene was chosen as a mediator from the point of view of availability. It was found that in the presence of naphthalene when the similar electrolysis as above (direct electrochemistry) was carried out, chlorobenzene was completely reduced to benzene after 6 F/mol of current was passed. This result indicates that the use of mediator for reduction of chlorobenzene is very efficient. It was also found that electrolysis at low temperature at 60 mA/cm^2 with platinum as a cathode and zinc as an anode is the optimum conditions in this case.

Conclusion

Electrolysis of chlorobenzene in DMF solution in the presence of naphthalene as mediator allows a complete dechlorination of the chlorobenzene and the formation of benzene as the only product. Current efficiency is closed to 100%.

References

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